The Boiling-point of Sulphur on the Constant-pressure Air Thermometer.

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The following experiments were undertaken at the suggestion of Professor Callendar, with a view to the redetermination of the boiling-point of sulphur (S.B.P.) on the scale of the constant-pressure air thermometer. The experiments unfortunately have not led to a result that can be regarded as final, owing to the uncertainty in the expansion of the glass, but it has been thought desirable to publish the results.*

The air thermometer was made of Jena glass, 16 III, and is in construction substantially the same as that described by Callendar.† Fig. 1 will make clear the form of the apparatus, and is drawn roughly to scale.

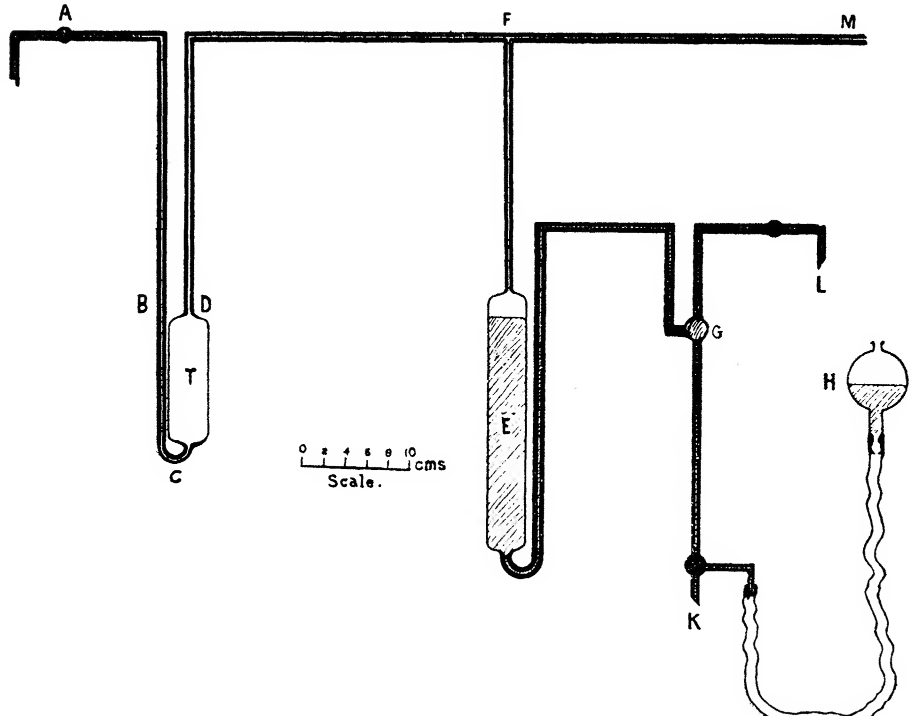

Fig. 1.

* All measurements of length are given in centimetres, and all measurements of volume in grammes of mercury at 0° C.

† H. L. Callendar, 'Roy. Soc. Proc.,' vol. 50, p. 247; 'Ency. Brit.,' "Thermometry."

T is the bulb to be heated, and is connected by capillary tubes on the one side to a tap A, and on the other to a second bulb E and by M to the gauges, which will be described shortly; E itself is connected to an inlet for mercury at L and an outlet at K. The reservoir H is convenient in setting up the apparatus, but is not used in the actual experiments. There is a small air-trap at G, in case air is accidentally introduced in manipulation through K or L. This part of the apparatus which contains the bulb T may be termed the thermometric side (T side).

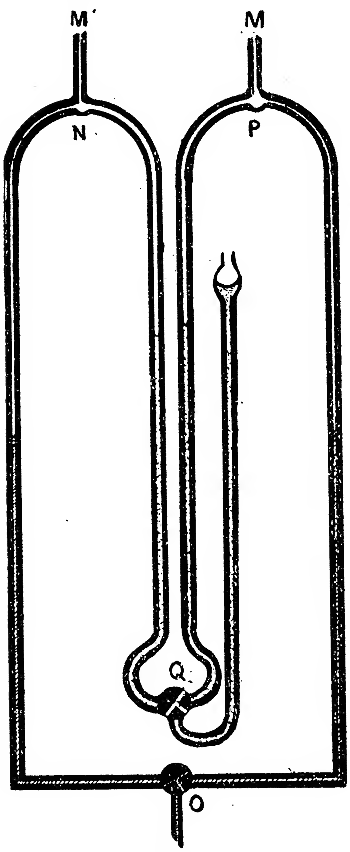

Fig. 2.

Alongside the above, and quite close to it, is an exactly similar system of tubes, except that the bulb T is missing, so that the capillary tube passes straight across from D to B (instead of down to C), and thence to a stopcock alongside A. This second system can be called the compensation side (C side), and contains a bulb similar to, and alongside, E.

The two systems are connected together by the gauges, which are represented in fig. 2. NOP is a mercury gauge for the rough adjustment of the pressure, while NQP is an oil gauge for the fine adjustment. O and Q are three-way stopcocks. It should be added that the plane of fig. 2 is at right angles to that of fig. 1.

In an actual experiment the air in T is limited in the direction of A by a thread of mercury which occupies part of the horizontal tube, in the direction of the gauges by the mercury and oil they contain, while E, which is always immersed in ice along with the corresponding bulb on the C side, contains a variable amount of mercury; the latter occupies also the capillary tubes to the outlets at H, K, and L. It is by varying the amount of mercury in E that the pressure on the T side is always adjusted to a certain standard, this standard being the pressure of the air on the C side in the bulb corresponding to E. It is thus unnecessary to read the barometer for this purpose. The mass of air on the C side is made as nearly as possible equal to that on the T side. If now the capillary tubes on the two sides are of the same temperature and volume at corresponding points, they exactly compensate

one another, as will be shown later. As, however, it is impossible to make the volumes absolutely equal, a rough measurement of the temperature is all that is necessary.

It will be noted that there is either mercury or oil at all the stopcocks; they are thus not assumed to be gas-tight. The diameter of all the connecting tubes is approximately 0·1, except that of the oil-gauge, which is 0·2. The latter was read by means of a microscope containing in the eye-piece a scale divided to 0·01; differences of pressure were thus read to 0·001 cm. of oil such as is used in a Fleuss pump. The weighings were made to the nearest milligramme. In order to ensure the delivery of mercury being accurate to this, the open end of each delivery tube was slightly constricted, the tube cut off at 45° to the axis at the narrowest part, and the end ground. The concordance of the results obtained when determining the expansion of the glass indicates that the delivery of mercury is probably accurate to 1 milligramme (1 in 360,000 on the F.I.).

It has already been stated that the oil in the oil gauge was that used in a Fleuss pump. The fact that it can be so used indicates that its vapour-pressure must be very low. For additional security a flask containing a sample of this oil was heated to 100° C. and kept evacuated for some time to remove any lower boiling substance that might be present. In this operation it was found that the oil dissolves a very small, though appreciable, quantity of air. The density of this sample was determined at 10° C. and at 20° C.

Development of Formula.

In the course of an experiment the two bulbs E are always kept at 0° C., or T_0 absolute. The bulb T is heated to any required temperature T. No change whatever is made on the C side, but on the T side mercury is added or removed, until the pressures on the two sides are as nearly as possible equal, any residual difference being read on the oil gauge by the microscope already referred to.

C side.—

Let the volume of gas in the bulb E = S, this at temperature T_0 (absolute),
" " connecting tubes = v, " " θ "

then
$$\frac{S}{T_0}+\frac{v}{\theta}=\frac{mR}{p},$$

where m = mass of gas and p its pressure, R being the usual gas constant.

T side.—

Let the volume of gas in the bulb T = V at temperature T (absolute),
" " E = Q " T_0 "
" connecting tubes = $v+\delta v$ " θ "

Let the mass of the gas $= m+\delta m$, and its pressure $= p+\delta p$,

then $$\frac{V}{T}+\frac{v+\delta v}{\theta}+\frac{Q}{T_0} = \frac{m+\delta m}{p+\delta p}R = \frac{mR}{p}\left(1+\frac{\delta m}{m}-\frac{\delta p}{p}\right)$$

approximately, as δm and δp are very small quantities.

Subtracting the former expression from the latter, we get

$$\frac{V}{T} = \frac{S-Q}{T_0}+\frac{R}{p}\delta m-\frac{mR}{p^2}\delta p-\frac{\delta v}{\theta}.$$

When obtaining the freezing-point of water (W.F.P.), the bulb T is surrounded by ice. Let us call the corresponding quantities δp_0, δv_0, θ_0 (note that the latter is not 0° C.). Then, as p remains practically constant,

$$\frac{V_0}{T_0} = \frac{S_0-Q_0}{T_0}+\frac{R}{p}\delta m-\frac{mR}{p^2}\delta p_0-\frac{\delta v_0}{\theta_0}.$$

We thus obtain the following equation:

$$\frac{V}{T} = \frac{V_0}{T_0}-\frac{Q-Q_0}{T_0}+\frac{S-S_0}{T_0}+\frac{mR}{p^2}(\delta p_0-\delta p)+\frac{\delta v_0}{\theta_0}-\frac{\delta v}{\theta}.$$

It will be noticed that the term involving δm has disappeared from this equation. It is necessary, however, that δm should be small, otherwise the compensation will be inaccurate.

Multiply throughout by ρ, the density of mercury at 0° C., so as to convert volumes into weights of mercury; we thus get, with an easily understood notation,

$$\frac{W}{T} = \frac{W_0}{T_0}-\frac{w}{T_0}+\frac{(S-S_0)\rho}{T_0}+\frac{mR\rho}{p^2}(\delta p_0-\delta p)+\left(\frac{\rho\delta v_0}{\theta_0}-\frac{\rho\delta v}{\theta}\right).$$

Writing this equation, for shortness, in the form

$$\frac{W}{T} = \frac{W_0}{T_0}-\frac{w}{T_0}+A+B+C,$$

we have finally

$$\frac{t}{T_0} = \frac{(W-W_0)+w-(A+B+C)T_0}{W_0-w+(A+B+C)T_0},$$

where $t \equiv T-T_0$, and is the temperature on the scale of this gas thermometer.

To obtain the coefficient of expansion of the gas, or its reciprocal T_0, after observing the W.F.P., the bulb T is surrounded with steam, thus giving the boiling-point of water (W.B.P.). t is thus approximately 100, while the right-hand side of the equation contains known quantities. We can hence calculate T_0. In obtaining the S.B.P. the converse of this process is gone through, T_0 being now known, while t is calculated.

The volumes of the connecting tubes, etc., were obtained by finding the quantity of mercury required to fill them. When the weight exceeded a few

grammes, weighings were made in both pans, and a buoyancy correction applied.

The following remarks will indicate the corrections that have been applied to the various terms of the above equation:—

(i) W_0.—This depends slightly on the height to which the ice is piled, as the two sets of tubes do not exactly compensate one another.

(ii) W.—Besides the correction mentioned in (i), allowance has to be made for the expansion of the glass. This will be discussed later.

There may be a small pressure correction to apply to W_0 and W owing to variations of the *external* pressure. This, however, never amounts to more than 2 or 3 milligrammes.

(iii) w.—The weight of the mercury in E causes this bulb to expand. As, therefore, mercury is removed, the bulb contracts. The correction due to this pressure effect amounts to 4 milligrammes for the W.B.P., and to 8 for the S.B.P. There is no external pressure correction, as this effect is compensated.

(iv) A.—As the two air-traps G (of fig. 1) are not exactly of the same volume, S may on this account differ from S_0. This correction is, however, quite small, a change of temperature of 10° being equivalent to 6 milligrammes.

(v) B.—This does not call for any remark.

(vi) C.—This term depends on imperfect compensation of the tubes connecting together the various parts of the apparatus. The temperature was read at three points: one thermometer was placed just above BD (of fig. 1), another just above this at the bend, and a third between N and P (of fig. 2). The reason for this distribution is obvious. The first thermometer would be considerably affected by the heating of T, the second to a much smaller extent, and the third scarcely at all. Screens were, of course, placed at suitable points to minimise these corrections. The ends of the mercury threads at A (of fig. 1) were read, also the positions of the mercury and oil in the gauges, and the corresponding influence on δv allowed for. δv amounts to about 0·5 gramme, this being almost entirely due to the difference in volume of the junctions at N and P (of fig. 2). As these parts are at a considerable distance from T, the correction involved has little uncertainty attached to it.

This list of corrections is formidable only in appearance. The corrections are very small. Tables are easily calculated, and the working out of a result involves only a few minutes' work.

Sensitiveness of the Oil-gauge.

With the apparatus as used the following table gives the approximate values of the sensitiveness of the gauge:—

At 0° C. a change of pressure of 0·001 cm. of oil corresponds to a change of temperature of 0°·00032.
„ 100° C. a change of pressure of 0·001 cm. of oil corresponds to a change of temperature of 0°·00060.
„ 445° C. a change of pressure of 0·001 cm. of oil corresponds to a change of temperature of 0°·00220.
„ 1000° C. a change of pressure of 0·001 cm. of oil corresponds to a change of temperature of 0°·0070.

In other words, the sensitiveness diminishes with increase of temperature. This, however, is of no practical importance. The accuracy with which a temperature can be measured cannot be greater than the accuracy with which the fundamental interval has been determined. Thus, at 1000° C. the sensitiveness need only be 1/10 of that at 100° C., and this is nearly fulfilled, as the above table shows. When, in addition, one takes into account the difficulty of maintaining these high temperatures constant, it would appear that the sensitiveness is all that is necessary.

As regards the uniformity of the results, I think separate measurements of the coefficient of expansion should not differ from the mean by more than some 20 units, if the coefficient is expressed by six significant figures. This point will be again referred to when discussing the second series of experiments.

Pressure Coefficient of the Bulbs.

These are required, but only roughly, for some of the measurements. Thus, in finding the volume of the bulb T by filling it with mercury, the pressure of the latter produces an appreciable expansion of the bulb. This, of course, has to be allowed for. Again, in calibrating the apparatus (*i.e.* in finding the volume of the capillary tubes) it was necessary to have occasionally the bulbs full of mercury. It was therefore essential to allow for the changes of pressure produced by running out the liquid. Finally, in the ordinary use of the thermometer, a small correction is required, as has already been explained.

The pressure coefficient was determined by filling the bulb in question with mercury, and increasing or diminishing the internal pressure. The compressibility of the mercury has, of course, to be allowed for. The constancy of the coefficient obtained with both small and large changes of pressure affords a very good test of the presence or absence of small air bubbles.

The pressure coefficient for the two bulbs E was determined at 0° C.,

while for the bulb T it was determined at 0°, 100°, and 184° with the following results:—

An external pressure of 1 cm. produces at—

0° C.	a change of volume of		0·00095	gramme.
100° C.	„	„	0·00099	„
184° C.	„	„	0·00106	„

Volume of the Bulb.

Before any experiments were made the bulb T was heated for many hours in sulphur vapour to anneal it. This produces an unknown change of volume. In general, therefore, the volume was determined at the end of each series by filling with mercury at 0° C. Each determination of the S.B.P. involves, however, a small change of the volume. It was noticed, in fact, that more mercury is run out of the bulb E in heating up T from the W.F.P. than has to be reintroduced in cooling down. This difference has been taken as a measure of the change of volume. The justification for this lies in the fact that it leads to *nearly* consistent values for the coefficient of expansion, although a total change of volume amounting to nearly 1 in 1000 has to be allowed for in the second series.

There is, however, another method by which the volume of the bulb T can be measured. Suppose all the bulbs are in ice, while both bulbs E are full of mercury. Now run out from the bulb E on the C side a weight of mercury somewhat greater than the approximately known capacity of the bulb T, allowing dry air to take its place. From the bulb E on the T side run out the estimated difference of these two volumes, allowing air to take its place, the pressures on the two sides being equal. This can be tested with the oil-gauge. The C side now contains a known quantity of air. Now turning off the stopcocks to prevent the entry of any further quantity of air, run out from the bulbs E mercury so as to diminish the pressure on both sides. From a knowledge of the weights of this mercury, and the observation on the oil-gauge of any residual difference of pressure, it is evident that by an application of Boyle's law a value can be obtained for the volume of T. Any deviation of the gas from Boyle's law is, to all intents and purposes, compensated for. It must be remarked, however, that for a good determination by this method a much more accurate knowledge of the volume and temperature of the capillary tubes must be obtained than is required in the ordinary use of the thermometer. It is, perhaps, due to this that the results to be given immediately are not more closely concordant; unfortunately, owing to an accident to the bulb at the end of the experiment, the volume could not be checked by the weight method.

The following are the results obtained:—

First Measurement, filling with mercury—

January 11, 1900	1276·015	Mean, 1276·017.
„ 11 „	1276·016	
„ 26 „	1276·020	

Second Measurement, filling with mercury (after a further heating in sulphur vapour)—

March 19, 1900	1274·828	Mean, 1274·824.
„ 24, „	1274·831	
„ 30 „	1274·813	

Third Measurement, filling with mercury—

July 13, 1901 .... 1273·912.

The substantial accuracy of this was confirmed a few days later by a rough measurement, which gave 1273·90 (not carried out in ice).

After this the bulb was heated for some 15 hours to a temperature of 600° to 700° C.

Fourth Measurement, Boyle's law experiment—

June 24, 1903	1260·882	Mean, 1260·980.
„ 25 „	1260·831	
„ 25 „	1261·054	
„ 25 „	1261·035	
„ 26 „	1261·099	

It is possible that the above table represents the concordance that one is able to get. On the other hand, there seems to be a sudden change after the second measurement, and in this connection it should be noted that an error in a weighing would entail an error in all the subsequent estimations of the volume of the bulb. It would have been better to have used throughout for each side a single vessel containing mercury from which to run back into E, or *vice versâ*; this would limit the error caused by an erroneous weighing to the one experiment, but a loss of mercury by careless manipulation, if of unknown weight, would still affect all the subsequent determinations of the volume of the bulb. As regards the uncertainty introduced by an error in the volume of the bulb, calculation shows that a positive error of 1 in 10,000 in W_0 produces a negative error of 50 units in the coefficient of expansion (with six significant figures) and a negative error of $0^{\circ}{\cdot}055$ in S.B.P.

Fifth Measurement, filling with mercury (fresh bulb)—

July 11, 1906 .... 1265·391.

Coefficient of Expansion of Bulb.

The important question of the expansion of the bulb made of Jena glass, 16 III, must now be dealt with, and it will be found necessary to discuss the results in some detail. The expansion of unit volume for any temperature t, measured on the constant-pressure scale, will be expressed in the form

$$[a+b(t-100)]\,t.$$

The measurements were carried out by filling the bulb and the capillary tubes that lead to it with mercury and heating the bulb. The corresponding tubes on the C side were also filled, so as to compensate for the exposed stem of the thermometer. The calculations have been made, using the two available values for the absolute coefficient of expansion of mercury, viz., that due to Regnault as recalculated by Broch,* and that due to Chappuis.†

First Series of Experiments.—After the observation in ice, the bulb T was heated up to W.B.P. in a double-jacketed apparatus of the ordinary form. After a small correction due to imperfect compensation of the capillary tubes, we get for the quantity of mercury driven out the following values :—

Date.	Temperature.	Observed weight.	Calculated weight.
1900.			
January 8	100 ·165	19 ·857	19 ·856
" 8	100 ·165	19 ·858	19 ·856
" 8	100 ·168	19 ·858	19 ·856
" 25	100 ·331	19 ·883	19 ·888

The two first values, marked for the same temperature, represent the mercury removed on heating up to W.B.P., and introduced on cooling down again to W.F.P. This was frequently done, and will not be again referred to. The last column is calculated by taking

$a = 23974 \times 10^{-9}$, from Regnault's value for the expansion of mercury,
or $a = 24361 \times 10^{-9}$ " Chappuis' " " "

A set of values was also taken at intermediate temperatures, the bulb T being heated in a large water bath kept vigorously stirred. At the higher

* 'T. et M.,' vol. 2 (1883).

† 'T. et M.,' vol. 13 (1907). A small slip has occurred here in calculating the cubical from the linear coefficient of expansion of glass, so that the term in t^2 for mercury should be 0·000 000 002 847, instead of 0·000 000 002 951. It is this corrected value that has been used.

temperatures the water was covered with a layer of oil to prevent cooling by evaporation. When the desired temperature was nearly reached, the flame was turned a little lower, so as to get a very flat maximum temperature, time readings being alternately taken of the weight and of a platinum thermometer. The indications of the latter were converted to the constant-pressure scale by assuming 444·53 as the S.B.P. at normal pressure. This perhaps, is slightly inconsistent, as the results of this paper lead to a lower value. It was, however, deemed inadvisable to make a change at this point. Now the expansion of mercury is given on the constant-volume scale. It becomes, therefore, necessary to allow for this small difference between the two scales. This has been done in accordance with D. Berthelot's* formula.

Correcting as before for a small want of compensation in the exposed stem, we get the following table :—

Date.	Temperature on the—				Weight of mercury.
	Platinum scale.	Constant-pressure scale.	Constant-volume scale.	Normal scale.	
1900.					
January 20	19 ·717	19 ·478	19 ·470	19 ·465	3 ·931
" 9	20 ·613	20 ·366	20 ·358	20 ·353	4 ·130
" 10	26 ·944	26 ·647	26 ·637	26 ·632	5 ·372
" 22	31 ·001	30 ·678	30 ·669	30 ·663	6 ·169
" 9	40 ·404	40 ·040	40 ·029	40 ·022	8 ·053
" 10	45 ·353	44 ·979	44 ·968	44 ·961	9 ·021
" 22	47 ·943	47 ·566	47 ·555	47 ·548	9 ·531
" 24	73 ·896	73 ·605	73 ·597	73 ·593	14 ·667

In calculating the mean value of b from the above data, I have omitted the second and fifth values, which give abnormally high values of b. These two weights (the two experiments were carried out on the same day) are not independent of one another, as the second weight was obtained by adding to the first the mercury driven out in heating up from 20° to 40°. It is hence thought probable that some error has crept into the first value. It will, in fact, be seen from the next table that a diminution of both weights by, say, 20 milligrammes would bring both into line.

The above experiments lead to the following value for b :—

$$b = 10{\cdot}55 \times 10^{-9} \text{ (Regnault's mercury formula)},$$
$$b = 19{\cdot}70 \times 10^{-9} \text{ (Chappuis' " ")}.$$

* 'T. et M.,' vol. 13 (1907).

The second and fifth columns of the following table have been calculated, using the following formulæ for the expansion :—

$$\{23974 + 10{\cdot}55\,(t-100)\} \times 10^{-9}, \tag{i}$$

$$\{24361 + 19{\cdot}70\,(t-100)\} \times 10^{-9}. \tag{ii}$$

Weight of Mercury driven out.

Observed.	Calculated—				
	Regnault.		Chappuis.		
	Formula (i).	Formula (iii).	Formula (ii).	Formula (iv).	Formula (v).
3·931	3·928	3·918	3·932	3·943	3·916
4·130	4·106	4·096	4·110	4·121	4·093
5·372	5·365	5·353	5·369	5·382	5·349
6·169	6·171	6·158	6·175	6·190	6·153
8·053	8·038	8·023	8·039	8·056	8·015
9·021	9·019	9·005	9·020	9·038	8·996
9·531	9·533	9·519	9·533	9·551	9·508
14·667	14·669	14·667	14·665	14·684	14·651

The third, fifth, and sixth columns will be explained later.

Second Series of Experiments.

After this, the bulb was heated up for a long time in sulphur vapour. The volume diminished, as already explained, and later the following experiments were carried out:—

Date.	Temperature.	Observed weight.	Calculated weight.
1900.			
March 19	99·399	19·702	19·702
„ 19	99·399	19·702	19·702
„ 20	99·738	19·766	19·768
„ 30	100·115	19·841	19·841

The last column is calculated by assuming for the expansion of the bulb—

$$a = 23868 \times 10^{-9} \text{ (from Regnault's mercury)},$$
$$a = 24254 \times 10^{-9} \text{ („ Chappuis' „)}.$$

It will be noticed that heating has diminished the value of a. This has been noticed by other observers.

To obtain a better value for b, it was determined to heat the bulb to a higher temperature, and the vapour of boiling aniline seemed the most convenient for the purpose. The aniline was boiled in a beaker about 40 cm. high and 9 cm. diameter. The bulb, with the platinum thermometer in contact with it, was surrounded by a copper cylinder to stop radiation and prevent cooling by convection currents. This was also aided by placing two horizontal tin-plates, one immediately over the copper cylinder and the other a few centimetres above this. These plates were of nearly the same diameter as the beaker, and had five holes punched in them to allow the various tubes and platinum thermometer to pass through. A small asbestos umbrella was placed on the stem of the weight and of the platinum thermometer to prevent the condensed aniline trickling down the bulb. In addition, two or three layers of asbestos paper were wrapped round the beaker. Three experiments were carried out, between each of which the bulb was emptied and refilled :—

Date.	Temperature on the—				Weight of mercury.
	Platinum scale.	Constant-pressure scale.	Constant-volume scale.	Normal scale.	
1900.					
March 28	181·227	183·450	183·490	183·522	35·935
" 23	181·563	183·798	183·838	183·870	36·003
" 23	181·563	183·798	183·838	183·870	36·015
" 29	181·661	183·901	183·941	183·973	36·022
" 29	181·661	183·901	183·941	183·973	36·022

The mean values of b calculated from these experiments are:

$$b = 4{\cdot}20 \times 10^{-9} \text{ (from Regnault's formula)},$$
$$b = 23{\cdot}47 \times 10^{-9} \text{ (,, Chappuis' ,,)}.$$

We hence have the two following formulæ:

$$\{23868 + 4{\cdot}20\,(t-100)\} \times 10^{-9}, \tag{iii}$$
$$\{24254 + 23{\cdot}47\,(t-100)\} \times 10^{-9}, \tag{iv}$$

while, to show the change introduced by a variation of b, the following formula has also been used:

$$\{24254 + 10\,(t-100)\} \times 19^{-9}. \tag{v}$$

Columns corresponding to these formulæ have already been given in connection with the experiments between 0° and 100°. The following table gives the corresponding calculations for the aniline values:

Weight of Mercury driven out.

Observed.	Calculated.				
	Regnault.		Chappuis.		
	Formula (i).	Formula (iii).	Formula (ii).	Formula (iv).	Formula (v).
35·935	35·789	35·938	35·986	35·938	36·201
36·003	35·856	36·004	36·054	36·005	36·269
36·015	35·856	36·004	36·054	36·005	36·269
36·022	35·874	36·024	36·074	36·025	36·290
36·022	35·874	36·024	36·074	36·025	36·290

It will be noticed that Regnault's value for mercury makes b diminish with rise of temperature, while Chappuis' shows an increase. It is true that Chappuis carried out experiments only between 0° and 100° C. As, however, his formula contains the same number of terms as Regnault's, it seems reasonable to extrapolate it. We have evidence from other observers that b diminishes with temperature. Kamerlingh Onnes,* from experiments on the same kind of glass between $-182°$ and 100°, is quite sure of the fact. Experiments at the Reichsanstalt† between $-190°$ and 500° indicate this as a general law for all substances tried, such as glass, porcelain, metals, and alloys, the only exception being brass. No experiments, however, are given for this particular kind of glass between these temperatures.

Chappuis' values for mercury were obtained by a weight thermometer method in a tube of *verre dur*, the linear expansion of which was measured directly between two marks made on the tube itself. These marks were not, unfortunately, on the neutral fibres. But apart from this, when one takes into consideration the method by which the ends of a tube are sealed off so as to form a bulb, and the change in the coefficient of expansion that must result from this, it seems unjustifiable to calculate the cubical from the linear coefficient, unless the tube has been very thoroughly annealed. This does not appear to have been done; at all events, no mention is made of it. The value of the mean cubical coefficient of expansion obtained was

$$(21696 + 16{\cdot}49t) \times 10^{-9}.$$

This is in good agreement with a value obtained by Harker and Chappuis,‡

$$(21801 + 15{\cdot}536t) \times 10^{-9},$$

* 'Comm. Phys. Lab. Leiden,' No. 95*b*.

† 'Ann. der. Phys.,' 4. F., vol. 6 (1901), p. 36, and vol. 22 (1907), p. 631.

‡ 'Phil. Trans.,' A, vol. 194 (1900), p. 74.

which is, presumably, an independent measurement. On the other hand, the second term does not agree with a value obtained for the same kind of glass at the Reichsanstalt:*

$$(22252+10{\cdot}83t)\times 10^{-9}.$$

Experiments between 0° and 100° on Jena glass, 16 III, carried out at the Reichsanstalt, give for the mean coefficient,

$$\{24238+10{\cdot}71\,(t-100)\}\times 10^{-9}.$$

[t is here on the normal scale, but for this purpose the difference can be neglected.] The expansion was observed on the neutral fibres, but the glass had not been annealed, except that it was slightly softened with a Bunsen burner to straighten it. It will be noticed that the "b" term is in excellent agreement with the value (10·55) deduced from my experiments with Regnault's values. This agreement has led me to prefer the latter observer's values for mercury, especially as use has to be made of the 184° value; a fair conclusion seems to be that the question of the true coefficient of expansion of mercury must still be regarded as an open one. In calculating, therefore, the S.B.P., the following formula has been used:—

$$\{23868+4{\cdot}20\,(t-100)\}\times 10^{-9},$$

where t is expressed on the constant-pressure scale; but it is useless to disguise the fact that it leaves the true value of the S.B.P. still uncertain. To change b from, say, 5 to 20 will raise the temperature by about 1°·41, and to change a from 23,868 to 24,254 will raise the temperature by a further 0°·06.

Recovery of Zero.

It was interesting to see if any recovery of zero could be observed after the aniline points. Two sets of observations were taken; readings at the W.F.P. could only be taken about three quarters of an hour after the aniline point. Readings of the mercury on both sides are observed, and it is to the difference of the readings that attention must be paid, so as to eliminate emergent stem errors.

* 'Wiss. Abh. Reichs.,' vol. 2, p. 129.

March 27, 1900.—Put out flame (heating the aniline) at 12.15 P.M., cooled bulb rapidly, first with hot, then cold, water. Started piling the ice at 12.40 P.M.

12.55 P.M. readings	....	T side	9·15
		C "	9·43
1.15 " "	....	T "	9·14
		C "	9·42
2.30 " "	....	T "	9·12
		C "	9·41
4.45 " "	....	T "	9·12
		C "	9·40

The second set is as follows:—

March 29, 1900.—Put out flame at 3.40 P.M. Began adding ice at 4.10 P.M.

4.30 P.M. readings	....	T side	10·05
		C "	10·06
4.50 " "	....	T "	10·05
		C "	10·06
March 30, 1900.—			
11.50 A.M. "	....	T "	10·06
		C "	10·06

In the latter case in the course of 20 hours a contraction of the bulb equivalent to 0°·005 was observed. As, however, readings were only taken to 0·01, it is possible that even this is mere error of observation.

When dealing with the determination of the S.B.P., some evidence will be given indicating an appreciable change in the course of a day.

The Resistance Measurements.

As the S.B.P. was observed directly on the air thermometer, and not through the intermediary of the platinum thermometer, the latter was only used in obtaining the expansion of the glass, where the accuracy of the readings is of less importance. It, therefore, seems unnecessary to enter into any long description here. It may briefly be stated that the box used was one made by the Cambridge Instrument Co., and is similar to one already described by Dr. Chree.* The coils were all replaced by silver-soldered manganin coils annealed for about 10 hours at 140° C. Three extra coils were added, as the thermometer used had a resistance at 0° C. of about 10 ohms. The calibrated bridge wire was shunted, so that 40 cm.

* 'Roy. Soc. Proc.,' vol. 67, p. 6.

were equivalent to 0·1 ohm. The resistances were occasionally tested against each other. In making the measurements the galvanometer circuit is kept closed, while the slider is shifted, until no deflection is observed on reversing the key in the battery circuit. Such a point could always be obtained. To eliminate heating effects, this balancing point was obtained first with one cell, then with two in series. The heating effect in the second case was assumed to be four times that in the first. As the latter never amounted to more than $0^{\circ}{\cdot}025$, and later with a more sensitive galvanometer was much less, there is little uncertainty in the correction for the purpose required. Leakage in the thermometer was frequently tested for.

The Barometers.

It is, of course, necessary to read the barometer for calculating the W.B.P. and the S.B.P. Originally, a Hick's barometer constructed on Fortin's principle was used. This bears a Kew certificate, dated December, 1873, giving the correction as +0·005. The vernier reads to 0·01, but was estimated to 0·003. Later, a barometer was constructed, the design of which is due to Professor Callendar. The object is to get the whole barometer immersed in water, so as to ensure a true temperature correction. Fig. 3 will make clear its construction.

A and B are two platinum-iridium needles, about 7·8 cm. long, fused in the glass. Their difference of length was determined after fusion, but before this part was joined on to the barometer, so that it was not necessary to make the observations through the glass. The distance apart is about 76 cm. C is a small air-trap; D serves for evacuation, and is afterwards fused off. The tube E communicates by rubber and glass tubes with a vessel F containing mercury, and a graduated oil manometer G open to the atmosphere at H. The barometer and rubber tube are surrounded by a wide tube full of water, the temperature being read on two thermometers. F is surrounded by cotton-wool to prevent any rapid change of temperature; an obvious arrangement permits the pressure in F to be varied. The quantity of mercury in AB is adjusted, so that when one surface touches the lower point of A the other should be practically touching B. The process of reading the barometer consists, then, in bringing the surface of the mercury first into contact with A, then with B, and reading the manometer on each occasion. If, for this *small* adjustment, we can assume the tube at A to have the same diameter as the tube at B, the arithmetic mean of the two manometer readings will give accurately the difference between the barometric pressure and that due to a column of mercury equal in height to the distance between the lower points

of the needles. An electrical arrangement for the contact was first tried, but very soon the contact at B became very bad, and an optical adjustment was adopted in its place. This barometer was found to work very well, but in the course of a few years the mercury and glass at B became dirty, partly no doubt due to water vapour passing through the rubber tube.*

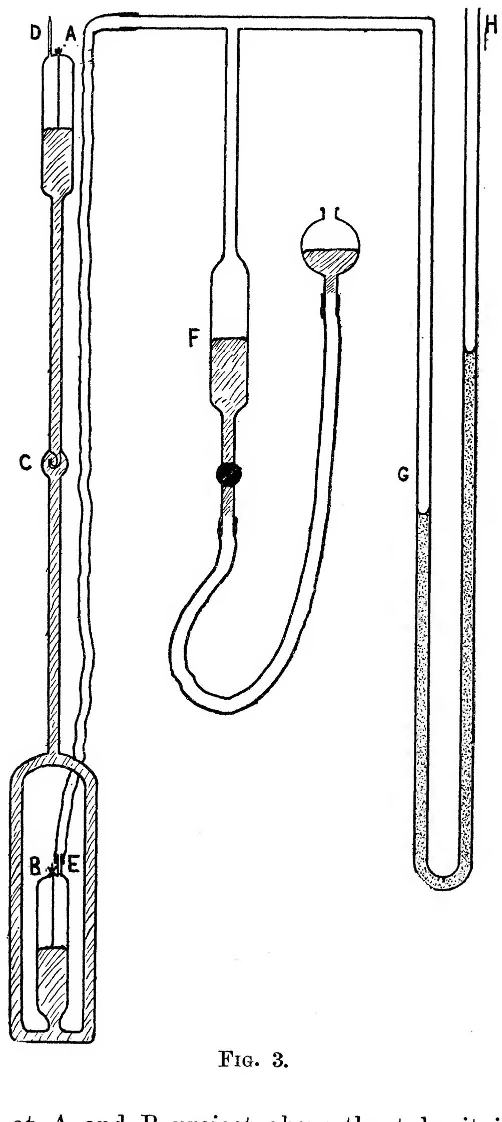

FIG. 3.

As the needles at A and B project above the tube, it is possible at any moment to verify the distance between them. This was done several times

* Compare Rayleigh, 'Coll. Pap.,' vol. 4, p. 42.

with a cathetometer, the scale of which was compared with an invar scale procured later:—

	Length at 11° C.
April, 1901	76·348
October, 1901	76·345
December, 1901......... ..	76·344

After the invar scale was procured, the length was compared directly with this:—

May, 1902	76·3462
December, 1906	76·3445

The invar scale was standardised once at Sèvres, and once at Teddington a few years later.

To obtain the coefficient of linear expansion, advantage was taken of a change of temperature in May, 1902:—

May 7, 8, and 9, 1902	76·3462 at 11° C.
May 27 and 28, 1902	76·3524 at 19°·3 C.

This is the length between the upper points, which were adjusted so as to be vertically one over the other. To obtain the distance between the lower points, three small corrections must be applied, one for the difference in length between the two needles, and the other two for the want of verticality of each needle.

The Hicks barometer was compared with this later one, and the correction for the former found to be +0·007. As the vernier only reads to 0·01, the agreement with the value given by the Kew certificate (+0·005) was considered satisfactory.

A small correction, due to a difference in height between the reservoir of the barometer and the bulb of the air thermometer, was applied to the barometer readings. Further, in calculating the pressure due to a given column of mercury, g in the laboratory was taken as equal to $1·00058\ g_{45,0}$.

In addition to the above barometer, a compensated barometer was used, the construction of which will be seen from fig. 4 (Callendar's Patent, No. 10,456, 1891).

The tube AB contains dry air up to a level E. The annular space between AB and CD, and the tubes to the levels E and F, contain Fleuss pump oil. The tube F is open to the atmosphere. The tubes G and H, which are finally sealed off, are convenient for filling the apparatus. The assumption is made that the air in AB is at the same temperature as the oil in CD. Knowing the coefficient of expansion of the oil, the volumes of AB, CD and the tubes are calculated, so that a change of temperature only of the atmosphere should make no difference in the level of the oil in E, while a change of pressure as

measured on a mercury barometer should be magnified 10 times on the tube E, which is accordingly graduated to read changes of pressure. If the volumes of the bulbs are not quite in the right ratio, small pieces of glass rod

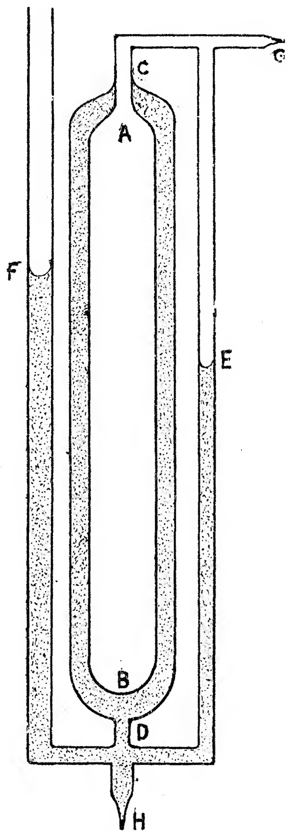

Fig. 4.

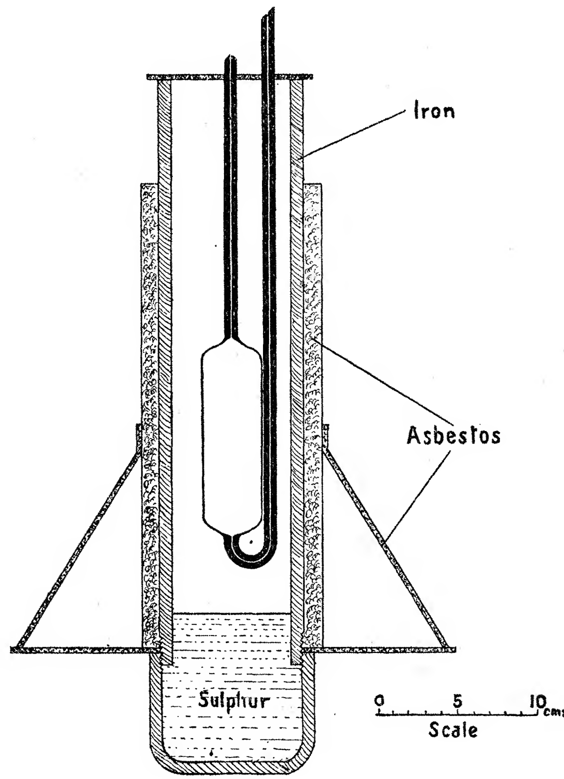

Fig. 5.

can be introduced through G or H to correct this. In practice, the standard barometer was read once during the day, and the changes of pressure in the course of a day read on the compensated barometer. A considerable saving in time was thus effected.

Course of the Experiments.

Only three temperatures were observed on the thermometer, viz., W.F.P., W.B.P., and S.B.P. For the W.F.P. the ice was obtained in $\frac{1}{2}$-cwt. blocks, washed with distilled water, and crushed very fine. The interstices were filled up with distilled water, or water from melted ice. Although the purity was occasionally tested with silver nitrate, this was, unfortunately, not done as a matter of routine. The W.B.P. apparatus was of the ordinary double-jacketed form. The lid of this was perforated for the various tubes, and leakage of steam

prevented by plugging with asbestos made into a pulp by moistening with a little water. No manometer was attached to this, as a similar hypsometer, but taller, and of smaller cross-sectional area, showed a practically negligible difference of pressure. The values of the W.B.P. are taken from Harker and Chappuis' paper.

The S.B.P. apparatus is shown in fig. 5 with the air thermometer in position (the tubes on the C side are omitted). The latter was sometimes accompanied by a platinum thermometer. To prevent radiation, the bulb was surrounded by a tinplate screen of the usual type (not shown), while above this two horizontal plates were placed (also not shown), almost closing the cross-section. These plates were, however, a source of much trouble. It was practically impossible to put them in place without scraping the sides of the glass tubes. This, after a time, always resulted in scratching, and later cracking, the tubes, and so putting an end to the experiments. Dr. Harker informs me that the prolonged action of sulphur vapour on the French *verre dur* is to make it very brittle. This can easily be shown not to be a mere temperature effect. The accidents may, of course, have been due to this.

In reducing the S.B.P. to normal pressure, the correction has been taken equal to $0{\cdot}88h$; no correction has been made for the pressure due to the sulphur vapour.

Some experiments were made to test the agreement of the S.B.P. obtained in a large and small iron boiler of the same type. The same platinum thermometer was immersed to the same height in both:—

Small Boiler. Diameter, 3·7.

July 16, 1903—			
No vertical screen, two horizontal discs......	pt. = 419·691	at	75·176
	= 420·328	„	76
July 17, 1903—			
A vertical screen „ „	pt. = 419·923	„	74·960
	= 420·726	„	76

Larger Boiler. Diameter, 7·6.

July 17, 1903—			
No vertical screen, two horizontal discs......	pt. = 419·548	„	74·960
	= 420·351	„	76
July 20, 1903—			
A vertical screen „ „	pt. = 420·861	„	76·125
	= 420·764	„	76
July 20, 1903—			
Two vertical screens „ „	pt. = 420·916	„	76·189
	= 420·770	„	76

The Experiments.

The bulbs and tubes were cleaned first with hot nitric acid, then hot potassium hydrate, then again nitric acid, and finally the whole apparatus was several times completely filled with distilled water. In the final drying, the bulbs C and E were at 100° C., while T was in sulphur vapour, and the whole apparatus repeatedly evacuated with a Fleuss pump. The thermometer was allowed to cool full of air at atmospheric pressure, and when cool it was finally evacuated and filled with air at 0° C. The air was purified by passing through a tube containing potassium hydrate, then sulphuric acid, and finally phosphorus pentoxide.

First Set.

March 9, 1900	W.F.P.		
		0·003 671 25	
	W.B.P.		
		0·003 671 18	
	W.F.P.		
		0·003 671 53	
	W.B.P.		
March 13, 1900	W.F.P.		
		0·003 671 63	
	W.B.P.		
March 14, 1900	S.B.P.		
	Diminution in volume of bulb = 0·610 gr.		443·47* at 76.
March 15, 1900	W.F.P.		
		0·003 671 15	
	W.B.P.		
March 16, 1900	S.B.P.		
	Diminution in volume = 0·246.		442·481 at 74·865 = 443·480 at 76.
March 17, 1900	W.B.P.		
		0·003 671 11	
	W.F.P.		

Mean coefficient	0·003 671 31
Final volume of bulb	1274·824
Pressure	76·7

* In this my first experiment with the large sulphur boiler, the evolution of vapour was so great that I turned the flame low—too low, in fact. The above temperature is obtained through the intermediary of the platinum thermometer which was alongside. The highest actual temperature measured was 443·495. The barometer on that day was 77·4.

Second Set.

June 25, 1901 ……	W.F.P.		
		0·003 669 86	
	W.B.P.		
June 26, 1901 ……	W.B.P.		
		0·003 670 42	
	W.F.P.		
		0·003 670 33	
June 27, 1901 ……	W.B.P.		
		0·003 669 85	
	W.F.P.		
		0·003 669 64	
June 28, 1901 ……	W.B.P.		
		0·003 669 74	
	W.F.P.		
		0·003 669 57	
	W.B.P.		
		0·003 669 63	
	W.F.P.		
July 1, 1901 ……	S.B.P.		
		Change of volume = 0·632	442·834 at 75·239 = 443·504 at 76.
July 2, 1901 ……	W.B.P.		
		0·003 670 37	
	W.F.P.		
July 3, 1901 ……	S.B.P.		
		Change of volume = 0·226	443·134 at 75·472 = 443·599 at 76.
	W.F.P.		
July 4, 1901 ……	S.B.P.		
		Change of volume = 0·148	443·909 at 76·209 = 443·725 at 76.
	W.B.P.		
		0·003 671 15	
July 5, 1901 ……	W.F.P.		
		0·003 670 28	
	W.B.P.		
		0·003 670 05	
	W.F.P.		
July 8, 1901 ……	S.B.P.		
		Change of volume = 0·181	444·130 at 76·480 = 443·708 at 76.
	W.F.P.		
		0·003 670 08	
July 9, 1901 ……	W.B.P.		
		0·003 670 65	
	W.F.P.		

Mean coefficient …………………	0·003 670 12
Final volume of bulb ……………	1273·912
Pressure …………………………	75·3

If the total changes of volume given above are added on to this final volume, it will make the initial volume greater than the final volume of the

first set. This, of course, is not impossible, as the bulb had a long time in which to recover. But the first set of coefficients is distinctly lower than the rest; it thus appears that the change of volume deduced is too large.

Now, as regards other variations observed in the coefficients. The second and third are both calculated from the same W.F.P. It is possible that the ice was not quite pure in this case, as the variation seems to exceed the experimental error.

On July 4, when a W.B.P. was taken immediately after a S.B.P., this coefficient comes out very large. The same effect will be noticed again in the fourth set. On July 8, a W.F.P. is taken just after a S.B.P., and the corresponding coefficient is smaller than the succeeding one, though the difference here is small. It is *as if* the bulb gets larger again; the effect may, of course, be due to something occurring in the gas. It should not be difficult to decide between the two explanations.

Third Set.

June 26, 1903 ...	W.F.P.		
		0·003 671 55	
	W.B.P.		
		0·003 671 26	
June 29, 1903 ...	W.F.P.		
		0·003 670 91	
July 1, 1903......	W.B.P.		
	S.B.P.		
	Change of volume = 0·147		444·201 at 76·611 = 443·842 at 76.
July 2, 1903......	W.F.P.		
		0·003 671 22	
July 3, 1903......	W.B.P.		443·920* at 76·170 = 443·770 at 76.
	S.B.P.		

Mean coefficient	0·003 671 23
Initial volume of bulb	1260·980
Pressure	76·0

In this case the volume was determined by the use of Boyle's law; it has not, therefore, the same claim to accuracy as in the other cases.

* This is deduced from the preceding W.F.P., the experiments having come to a conclusion at this point, owing to an accident.

Fourth Set.

Date	Observation	Coefficient	Result
June 21, 1906	S.B.P.		444·179 at 76·739 = 443·529 at 76.
	Change of volume = 0·174		
June 22, 1906	W.B.P.	0·003 671 06	
	W.F.P.		
June 27, 1906	S.B.P.		443·472 at 75·843 = 443·610 at 76.
	Change of volume = 0·012		
	W.B.P.	0·003 671 76	
June 28, 1906	W.F.P.	0·003 670 18	
	W.B.P.		
	S.B.P.		443·140 at 75·490 = 443·589 at 76.
	Change of volume = 0·080		
June 29, 1906	W.F.P.		

Mean coefficient	0·003 670 62
Final volume	1265·391
Pressure	76·2

The mean coefficient is that derived from the first and last; the second has been omitted for reasons that have already been referred to. If the mean of the three had been taken, the S.B.P. would be lower by 0°·06. On June 27, after the W.B.P., an attempt had been made to obtain a W.F.P. Owing to want of time, it was considered unsatisfactory and cancelled the same evening. If any reliance can be placed on the observation, there was a diminution of pressure by the next day of 0·002 cm. mercury, and the W.B.P. was taken before this; it is obvious, then, what a serious error must arise owing to the uncertainty as to the behaviour of the glass.

Eleven values of the S.B.P. have thus been obtained, the lowest of which is

443·47,

and the highest 443·84.

The mean is 443·62;

while, if we miss out the third set as being less reliable, the mean is

443·58.

In conclusion, I must express my indebtedness to Professor Callendar for constant help during the progress of the experiments; I have also to thank Dr. C. E. Guillaume for advice in procuring and standardising the invar scale.